Fluoride Pollution and its Control in Mining Areas

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Fluoride Pollution and its Control in Mining Areas

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CERTIFICATE

This is to certify that the thesis entitled "**Fluoride Pollution and its Control in Mining Areas"** submitted by **Mr. Suman Sourav** (Roll no. 215MN1442); in partial fulfilment of the requirement for the award of Master of Technology Degree in Mining Engineering at the National Institute of Technology, Rourkela; is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any University/Institute for the award of any Degree or Diploma.

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DECLARATION OF ORIGINALITY

I, **Suman Sourav**, Roll number 215**MN1442,** hereby declare that this thesis entitled **"Fluoride Pollution and its Control in Mining Aeas"** represents original work carried out by me as a post-graduate student of NIT Rourkela and to the best of my knowledge, contains no material previously published or written by another person, nor any material presented by me for the award of any other degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela, is explicitly acknowledged in the thesis. Works of other authors that are cited in this thesis have been acknowledged under the sections **References**. I have also submitted my original research record to the scrutiny committee for the evaluation of my research work.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present thesis.

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ABSTRACT

Fluoride is also found in natural water at some concentration level. In seawater, fluoride is found 1 mg/l. In river and lakes, less than 0.5 mg/l. of fluoride is found and high concentration of fluoride occurs in groundwater. According to Indian standard drinking water specification and WHO, the maximum permissible limit of fluoride in drinking water is 1.5 ppm and highest desirable limit is 1.0 ppm. Fluoride has an advantageous effect on teeth at low concentration in drinking water. However, at high concentrations it has adverse effect on health. Excessive amount of fluoride ingested for a long period by human being causes a crippling disease known as fluorosis, which is not curable. The crippling skeletal fluorosis cause increases morbidity in a number of regions in the world. A number of studies have been done which shows an acute effect due to overdose of fluoride exposure. Naturally, fluoride present in drinking water have long term effects due to exposure and other natural sources which is the major concern to human health.

Recently, there have been reports of increase in the concentration of fluoride in both surface and ground waters in and around Talcher Coalfield. Therefore, Talcher coalfield was chosen as a case study for the assessment and control of fluoride. The untreated waste water contaminated with fluoride discharged from industrial units are either allowed to accumulate in the lagoon or discharged to the river without adequate treatment. The water from the mining region mix with the Nandira and Bangaru nallah, finally terminating with Brahmani river. The ground water also gets contaminated by percolation through the soil. A large number of villagers have reported fluoride induced symptoms like pain in the lower leg. The domestic animals like castles have shown bone related problems in this region. While Talcher is among the worst affected, there are other districts where the problem has assumed serious proportions.

In the present study, a few locations in Talcher coalfield was selected for assessment of fluoride concentration. It may be noted that in this region, fly ash disposal is being carried out in some of abandoned quarries and mines sumps. One of the biggest problems due to disposal of large quantities of coal ash is the possible leaching of different hazardous pollutants, including fluoride. Therefore an attempt has been made to investigate the concentration of fluoride in the selected location and to find out their source. Additionally an attempt has been made to find out an effective treatment method as well as optimum dose for removal of fluoride from the collected samples.

In this study, removal of fluoride by coagulation process using Alum and Nalgonda technique; and adsorption by activated carbon was studied. The effect of each adsorbent has been examined and discussed. The effect of the coagulants on turbidity and pH were also studied. It was found that 100% of fluoride can be removed with 0.3gm/l of fluoride. In order to reduce the cost, the treatment can also be carried out with 0.1 gm/l of alum, since the fluoride concentration comes below the permissible limit after 1 hour of treatment.

Nalgonda technique is a simple and economical method for fluoride removal. It is addition of alum, lime and bleaching powder followed by rapid mixing, flocculation, filtration and disinfection. Aluminium is added to the sample and it is responsible for removing fluoride. Increase in alum when fluoride is increase. $1/20^{th}$ to $1/25^{th}$ of that of the dose of the alum is the dose of lime. Bleaching powder is added at the rate of 3 mg/l for disinfection. It is preferred over the rest because of its low price and ease with which it is handled. In the present case, it was seen that with addition of 0.3 g/l of alum, 0.001 gm of lime and 3 gm/l of bleaching powder, 100% removal of fluoride can be carried from both the ash pond and central sump water after one hour.

Activated carbon is a cost effective material, and is being used for widespread application including removal of different harmful contaminants present in water. It was seen that with the addition of 0.8g/l of activated carbon, the fluoride concentration comes below the permissible limit after 1 hour of treatment. The reduction in fluoride concentration thereafter is very minimal. Therefore o.8 g/l can be considered as the optimum dose for treatment.

A major finding of this study is the reduction of pH after treatment. In all the cases the pH concentration falls drastically, making the water highly acidic. This may cause acid mine drainage. The reason for such behaviour has not been found out. Therefore, while carrying out treatment of fluoride contaminated water in coal mining areas, the neutralization pH is also to be kept in mind.

Keywords: Fluoride contamination; coal mining, fly ash, leaching, coagulation, Nalgonda technique, adsorption, activated carbon

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Chapter 1

INTRODUCTION

1. INTRODUCTION

1.1 Background

Fluorine is part of the halogen group and is the reactive of all chemical elements. It is an electronegative element and has strong tendency to acquire negative charge, and forms F^- ions in solution. Fluorine is found as fluorides in environment which together represent about 0.06–0.09 per cent of the earth's crust. The average crustal abundance is 300 mg/kg. It is found in several minerals, including fluorspar, rock phosphate, cryolite, apatite, mica, hornblende and others at significant levels. In sedimentary and igneous rocks, fluorite (CaF_2) is a common fluoride mineral of low solubility occurring in both. Fluoride is usually associated with volcanic activity and fumarolic gases (Fawell and Bailey, 2006).

Fluoride is also found in natural water at some concentration level. In seawater, fluoride is found 1 mg/l. In river and lakes, less than 0.5 mg/l. of fluoride is found and high concentration of fluoride occurs in groundwater. According to Indian standard drinking water specification and WHO, the maximum permissible limit of fluoride in drinking water is 1.5 ppm and highest desirable limit is 1.0 ppm (WHO, 1984 and IS, 10500). Concentration of fluoride greater than 1.5 ppm in drinking water causes dental fluorosis and a higher concentration causes skeletal fluorosis (Fawell and Bailey, 2006).

Igneous and metamorphic rocks are associated with high groundwater fluoride concentration. Granites and gneisses rocks from India, Pakistan, China, Sri Lanka, West Africa, Thailand and Southern Africa have been reported with high fluoride concentration. In dry zone of Sri Lanka fluoride concentration of up to 10 mg/l are associated with dental and skeletal fluorosis. It has been recorded that high fluoride concentration has been found in-geographical belts which are of marine origin in mountainous area, volcanic rocks and granitic and gneissic rocks. The very first example is from Iraq and Iran through Syria and Turkey to the Mediterranean region and from Algeria to Morocco. It comes from the southern parts of the USA, southern Europe and the southern parts of the former USSR.

In India, epidemic fluorosis is a bit challenging and widely studied national health problem. It was reported in 1991 that, out of 32 states and 7union territories in India 13 states were naturally affected by high concentrations of fluoride in water but the number rose to 17 by

1999. Most seriously affected areas are Punjab, Andhra Pradesh, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh. High concentration of fluoride is observed in India in Rewari District of Haryana which is 48 mg/l (Fawell and Bailey, 2006).

Rajiv Gandhi National Drinking Water Mission solves the problem of fluoride in rural areas, with great support from external agencies, particularly UNICEF. However, even with the great interest in fluoride in India, it is not easy to arrive at an accurate or reliable estimate of the number of people at risk. This is because of the difficulty of sampling groundwater from India's many millions of hand pumps. Existing sampling are selective but unstructured, taking some villages from districts and some of the many pumps in each village (UNICEF, 1999).

An investigation of water quality in Angul district of Orissa in 2013 revealed that the pH of ground water varied from 6.4 to 7.5 and 5.3 to 9.2 in summer and post-monsoon respectively. The ground water is slightly alkaline condition in most of the cases. This favours the dissolution of fluoride bearing minerals in ground water. The concentration of fluoride was found in the range of 0.2 to 2.1 mg/l in summer and 0.4 to 2.4 mg/l during post-monsoon season. It is believed that alkaline condition of ground water favours the solubility of fluorine- bearing minerals while in acidic medium (acidic pH), fluoride is adsorbed in clay. However, in alkaline medium, it is desorbed, and thus alkaline pH is more favourable for fluoride dissolution activity. Ground water fluoride concentration is very high during post monsoon season indicate the result of anthropogenic activities in the study area. Because of seepage, moving and percolation of fluoride contaminated effluents from nearby existing industries such as Aluminium smelter and Talcher Thermal Power Plants. Leaching from ash pond after rain also contributes to the higher concentration of fluoride in ground water (Prasad, 2007). The concentration of fluoride is 27.8% in summer and 38.9% in post-monsoon season of the groundwater which exceeds the desirable limits of fluoride (1.0 mg/l) prescribed for drinking purpose by Indian and WHO standard. The study revealed that rock-water interaction is the major source of fluoride in ground water and very much influenced by local lithology. But in post-monsoon season, besides the weathering processes, anthropogenic activities also play a significant role in the incidence of fluoride in ground water (Reza & Singh, 2013).

In the present study, a few location in Talcher coal field was selected for assessment of fluoride concentration. It may be noted that in this region, fly ash disposal is being carried out in some of abandoned quarries and mines sumps. Therefore an attempt has been made to investigate the concentration of fluoride in the selected location and to find out their source. Additionally an attempt has been made to find out an effective treatment method as well as optimum dose for removal of fluoride from the collected samples.

1.2 Objective of Research

Keeping the above problem in mind, this work has been planned to study assessment of fluoride contamination and defluoridation behaviour of different reagent in Talcher Coalfield. The specific objectives are:

- Determination of fluoride concentration in selected locations of Talcher Coalfield.
- Assessment of fluoride concentration in fly ash.
- Assessment of defluoridation behaviour using different reagents.
- Selection of appropriate reagent and optimum dose for defluoridation.

1.3 Methodology

To achieve above objective, fly ash and water samples were collected from different parts of Talcher Coalfield. Coagulants for this project have been selected based on the study of past literature, their availability and cost. The concentration fluoride in water sample was detected by Ion Selective Electrode to find out whether fly ash is responsible for fluoride generation. To determine the fluoride concentration from fly ash the different techniques are used like Standard EN 12457-2 leaching test, standard HJ 557 2010 leaching test. The above two leaching tests were used in the study to find out the fluoride concentration from fly ash. Once the fluoride concentration is determined, the reagent for its treatment was selected based on the study of the past literature the availability and cost, a series of experiments was carried out to study their behaviour in removing the fluoride from collected samples while performing the experiment the pH as well as fluoride content was also continuously measured.

Chapter 2

LITERATURE REVIEW

2. LITERATURE REVIEW

A lot of research has been carried out by different researchers. Summary of some of the relevant research has been presented here.

Pickering (1985) studied the fluoride release in the soil, fluoride adsorption by soil and leaching. The role of chemical equilibria has been considered, through analysis of chemical interactions which involves fluoride species and soil components such as clays, hydrous oxides (Al, Fe, Mn), organic matter, calcite and quartz.

Brizendine et al. (1995) tested low level of fluoride on four groups of rat's by adding 0, 5, 15, or 50 ppm fluoride in their drinking water. The animals died after three, six, twelve, or eighteen months of treatment. The Animals that died after 18 months were examined with the bone marrow on sister chromatid exchange (SCE). They observed that the mineralized tissue fluoride concentration and the total fluoride in the carcasses increased continually as the animals aged.

Sujana et al. (1998) used alum to fluoride removal from aqueous solution. Treated alum sludge surface sites are heterogeneous in nature as evident from the data. For complete removal of fluoride from aqueous solution the optimum pH was found to be 6.The adsorption rate was fast during the initial 5 minutes, and takes 240 minutes to reach the equilibrium. The influence of addition of anions for fluoride removal depends on the relative affinity of the anions for the surface and the relative concentrations of the anions.

Piekos and Paslawska (1999) reported the problem of high fluoride concentration in drinking water in upper regions of Ghana. They used fly ash for removing heavy metals and radionuclides from aqueous solutions. Slurry was prepared from 10 gram of fly ash and 100ml water had a pH of 10.1. At 20°C sorption experiment was conducted in a column packed with 450 gram of fly ash. 1, 5, 10, 20, 50 and 100 mg/l concentration of fluoride in water fed on the column. 250 ml of fluoride solution poured onto the column to moisten the fly ash. Fluoride solution (250 ml) was placed in the top reservoir and the draining rate was 2.0 ml/hr. it conclude that a double mechanism is likely to operate in the retention of fluoride by fly ash: chemical binding by calcium hydroxide and physical sorption by residual carbon partices.

Mjengera and Mkongo (2003) used alum/lime method, bone-char method and the combination of two methods for defluoridation in ground and surface water in different parts of Tanzania. Wood charcoal was used in bone char method, bone char particles sizes were

studied for fluoride removal. The fluoride concentration is less than 0.1mg/l which was initially 12.0mg/l when using bone char media.

When Alum and Lime method was used for fluoridation early fluoride of 12mg/l was found which reduced to 2 to 3mg/l. The bone char method is appropriate in rural area of Tanzania because of its simplicity, local availability of materials.

Bhattacharya et al. (2004) described an adsorption method to remove the fluoride from the groundwater, present in hard rock areas in the south of the Ganges valleys & north-western part of the country. Because of Precipitation of calcite, Ca activity lowers and hence increases Na/Ca ratios, this causes increase in fluoride levels. Dolomite controls the Mg in the southern India, while palygorskite and sepiolite are Mg sinks in Rajasthan but they release fluoride under alkaline conditions. The last two minerals are likewise essential sources and sinks for Fluoride in the hydroxy-positions.

Ghorai and Pant (2005) used activated alumina for removing fluoride. Langmuir equation was used for the adsorption isotherm and isotherm constants. The adsorption of fluoride depends on the pH of the solution and is used to achieve the optimum pH value and a helps in the better understanding of the adsorption mechanism. It was seen that maximum adsorption takes place at pH value of 7. Analysis showed that early saturation and fluoride removal takes place at higher flow rate and at higher concentrations. Predicted simulation results are one-dimensional model for isothermal, axially dispersed fixed bed. Bed depth service time (BDST) model was also applied successfully.

Maheshwari (2006) has presented a review on sources of fluoride, ill, effects and techniques for fluoride removal in India. Defluoridation technique of activated alumina is used in several villages Sarita Sansthan, Udaypur, Rajasthan for removing the fluoride in drinking water. In activated alumina process can remove up to 90%. In ion exchange it can be up to 90-95%. Nalgonda technique is used in Nagpur in rural areas it is an effective technique for fluoride removal, 18-33% a smaller portion of fluoride removed in the form of precipitate and a greater portion of ionic fluoride (67–82%) is converted into soluble aluminium fluoride complex ion, and therefore this technology is inaccurate. In RO, fluoride removal efficiencies up to 98%. It is conclude that efficiency of fluoride removal vary according to many site specific chemical, economical and geographical conditions.

Gopal et al. (2006) used an alum-impregnated activated alumina (AIAA) for defluoridation, and found that 99% fluoride is removed from water at pH6.5. The result of Energy-dispersive

analysis of X-ray clear that the take-up of fluoride at the AIAA/water interface is because of just surface precipitation.

Suneetha et al. (2008) used alum and lime is at different concentration level using Nalgonda technique. The combination of alum (1000 mg/l) and lime (60 mg/l), fluoride level before treatment is 5.6 and after treatment is 1.4 in tap water and in drinking water fluoride level before treatment is 2.3 and after treatment is 0.27. This combination shows that treatment of alum and lime the concentration of fluoride diminished by 75% in tap water and 88.2% in drinking water. It is notice that increasing the average pH level is increases in tap water from 7.4 to 7.6 and decrease in drinking water from 7.3 to 7.1.

Emmanuel et al. (2008) studied the behaviour of commercial activated carbon and indigenously prepared activated carbons (IPACs) from Pithacelobium dulce, Ipomoea batatas and Peltophorum ferrugineum for adsorption of fluoride. The preparation of activated carbon , the raw material carbonised at 300^{o} C. 40 gm of activated carbon powder 400ml HNO_3 were taken into 1000 ml conical flask and then mixture is gently heated to boiling for 20 minutes. It is filtered and thoroughly washed with double distilled water. The results of the experiments have shown that the percentage of fluoride removal has increased with the increase of contact time and dose of adsorbent. On the contrary the percentage of removal has decreased with the increase in initial concentration of the standard fluoride solution. The results suggest that intra-particle adsorption is very important in adsorption process.

Malik (2013) observed that is disposal of coal ash may leach different pollutants including fluoride. A solution of pH 4.2 a batch leaching study was carried out. Leaching was done at 1:20 ratio solid to solution ratio. 40 ml solution of pH 4.2 was mixed with 2 gm of fly ash and was continuously stirred . Fluoride leaching is a serial leaching the concentration of fluoride decreases with increase in contact time.

Reza and Singh (2013) investigated the fluoride occurrence in Angul district, Orissa. They collected samples from open wells and tube wells of 18 groundwater samples for determining the fluoride and others parameter. The study revealed that rock-water interaction is the major source of fluoride in ground water and influenced by local lithology. But in post-monsoon season, besides the weathering processes, anthropogenic activities also play a significant role in the occurrence of fluoride in ground water thus it concludes that high fluoride concentration in ground water during post-monsoon season is because of seepage and percolation of fluoride in contaminated water near industrial complexes.

Pandey et al. (2013) reported the deterioration of ground water due to fluoride in some part of Chhattisgarh state. Analysis of fluoride was done by ion selective electrode. Kolam, Muragaon and Saraitola of ground water content high fluoride up to 7.0 ppm. Range of 1.0-1.2 ppm in Basanpalli, Bhalumuda, Dolesara, Penkapara, Kunjhemura villages. In Raigarh-Sarguja has significant amount of fluoride in the ground water because of increasing coal mine actives in the region.

Ayoob et al. (2016) used Nalgonda technique for defluoridation. The dose of lime taken was 1/20th part of filter alum. 3mg/l bleaching powder was added to the raw water to ensure disinfection. It is a "fill and draw type" defluoridation technique is designed for community application, in India, 20-40 million gallon have been used for fluoride endemic areas.

Regassa et al. (2016) carried out batch mode study for fluoride removal from ground water and aqueous solution samples by natural coal. pH is 2 for optimal removal efficiency of fluoride when coal is physically and chemically activated and pH is 4 for natural coal. Maximum adsorption capacity of fluoride is 5.9, 8.36 and 11.35 mg/g for natural, physical and chemical activated coal in their order written from Langmuir model. The adsorbents from fluoride contaminated groundwater indicated that natural coal (NC), physically activated coal (PAC) and chemically activated coal (CAC) can be utilized as a powerful, ease adsorbent to removal of fluoride from groundwater.

Chapter 3

HEALTH IMPACTS OF FLUORIDE

3. Health Impacts of Fluoride

3.1 Sources of Fluoride

There are two main sources of fluoride, natural and anthropogenic sources which adverse impact on human, environment etc (Lennon et al., 2004).

Natural Sources

Soil: In soil, fluoride is present in the range of 150-400 mg/kg. Fluoride present in clay soil is about 1000 mg/kg because of phosphorous fertilizers fluoride present in soil.

Water: Less than 1 mg/l fluoride present in drinking water benefit for bone and teeth. Fluoride which is higher than 1 mg/l in drinking water causes dental fluorosis, skeletal fluorosis, crippling effects. Fluoride in ground water from the soil there are several factors which is responsible such as geological factors, nature of rocks, pH, consistency of soil and temperature of the soil, chelating action of other elements, depth of wells, leakage of shallow groundwater, and physical and chemical characteristic of water.

Forage, grasses and grains: higher level of fluoride is found near the industries compared to other area. Grasses and forages have higher level of fluoride than the industrialized area.

Volcanic activities: because of volcanic eruption animals and plants are being affected. Volcanic ash contains higher level of fluoride concentration as volcanic eruptions release hydrogen fluoride.

Anthropogenic sources: This is the main source of fluoride. Anthropogenic sources like phosphate fertilizer causes high fluoride near industries area which affect animal, groundwater, human etc.

3.2 Occurrence of Fluoride

Fluoride may be released into the environment either naturally or by human activities. Fluorides are released naturally into the environment by the weathering of rocks and through atmospheric emissions from volcanoes and seawater. Human Activities also release fluorides into the environment mainly through mining and processing of phosphate rock and as it is used as agricultural fertilizer, as well as the manufacture of aluminums. Other fluoride sources include the combustion of coal (containing fluoride impurities) and other

manufacturing processes (steel, copper, nickel, glass, brick, ceramic, glues and adhesives). The use of fluoride-containing pesticides in agriculture and fluoride in drinking water supplies also contribute to the release of fluorides to the environment (Pratap and Singh, 2013).

Fluoride content in surface water varies according to location and proximity to emission sources. Surface water concentrations generally range from 0.01 to 0.3 mg/liter. Seawater contains more fluoride than fresh water, with concentrations ranging from 1.2 to 1.5 mg/litre. Areas where the natural rock is rich in fluoride has higher fluoride content, and elevated inorganic fluoride levels are often seen in regions where there is geothermal or volcanic activity (25–50 mg fluoride/liter in hot springs and geysers and as much as 2800 mg/litre in certain East African Rift Valley lakes). Airborne fluoride exists in gaseous and particulate forms, which are emitted from both natural and anthropogenic sources. Fluoride released as gaseous and particulate matter is deposited in the general vicinity of an emission source, although some particulates may react with other atmospheric constituents. The distribution and deposition of airborne fluoride are dependent upon emission strength, meteorological conditions, particulate size and chemical reactivity. In areas not in the direct vicinity of emission sources, the mean concentrations of fluoride in ambient air are generally less than 0.1 $\mu g/m^3$. Levels may be slightly higher in urban than in rural locations; however, even in the vicinity of emission sources, the levels of airborne fluoride usually do not exceed 2–3 $\mu g/m^3$ (Pratap and Singh, 2013).

3.3 Impact on Human Health

Fluoride has an advantageous effect on teeth at low concentration in drinking water. However, at high concentrations it has adverse effect on health. Excessive amount of fluoride ingested for a long period by human being causes a crippling disease known as fluorosis, which is not curable. The crippling skeletal fluorosis cause increases morbidity in a number of regions in the world. A number of studies have been done which shows an acute effect due to overdose of fluoride exposure. Naturally, fluoride present in drinking water have long term effects due to exposure and other natural sources which is the major concern to human health.

3.3.1 Effects on Teeth

Fluoride has both advantages and detrimental effect on dental health when fluoride present in drinking water. If the fluoride present in drinking water which is consumed is minimum, then it is will reduce dental caries If higher concentration of fluoride is present in drinking water, it causes dental fluorosis. Generally 10 mg/l is related with dental fluorosis (yellowish or brownish striations or mottling of the enamel. In low level of fluoride (less than 0.1 mg/l) is related with dental decay. It means the fluorotic effect on teeth is minimum when fluoride is present in minimum level and it is harmful when fluoride is in high concentration. When fluoride is less than 1mg/l present in water than it is good for dental caries (Edmunds and Smedley, 1996).

For dental caries, the fluoride concentration in drinking water is 1mg/l. For children, lower level of fluoride (less than 1 mg/l) is important for dental caries. Higher level of fluoride concentration will result in dental fluorosis. In critical cases, the result in erosion of enamel. Small difference of fluoride concentration between beneficial effects of fluoride and occurrence of dental fluorosis and public health programmes seek to retain a suitable balance between the two (IPCS, 2002).

The level of dental caries (measured as the mean number of Decayed, Missing or Filled teeth) falls from 7 at a fluoride concentration of 0.1 mg/L to around 3.5 at a fluoride concentration of 1.0 mg/L. Dental decay continues to fall, but slowly when fluoride (up to 2.6 mg/l) concentration increases. When fluoride concentration increases than the dental fluorosis also increases. The fluoride concentration at 1 mg/l a 20 percent of children has evidence of dental fluorosis. Thus the evidence suggested that, the fluoride level in temperate climate is around 1 mg/l naturally present in water (Dean, 1942; USPHS, 1991).

Pitting of teeth is a cosmetic effect because of dental fluorosis .Due to raised fluoride level it develops a enamel. Thus, dental fluorosis can develop in children but not in adults. High fluoride exposure in a when the adult was a child or teenage.

The first reports on the dental fluorosis occurrence in 1888, from Durango in Mexico described as “black teeth’’. Afterwards, erosion of enamel was described amongst inhabitants of Naples in 1891 and in Italian migrants to the USA towns near Naples. Afterwards, in the early 1900_s in the several location in the USA (Black and McKay,1916; Fleischer, 1962). Fluorosis is widespread health problems in many countries all around the world suggested by Belyakova and Zhavoronkov (1978).

3.3.2 Skeletal Fluorosis

Skeletal fluorosis is said to be more endemic in regions of India, China and northern, eastern, central and southern Africa. It is caused due to drinking water containing high level of fluoride but exposure to sources of fluoride such as fluoride coal is potentially very viable. They are accelerated by a various factors like climate, water consumption, nutritional level and diet. Crippling skeletal fluorosis, which is related to higher levels of exposure, can result from ligament calcification and extreme bone deformity. Due to exposure to increased concentrations of fluoride causes skeletal fluorosis (IPCS, 2002).

One of symptoms of fluorosis is bone fracture. However, some studies have reported a protective effect of fluoride on fracture. All fractures, follows a U shaped dose response with higher rates of fracture at very low intakes below 0.34 mg/l and high intakes above 4.32 mg/l (total intake 14 mg per day) (Li et al., 2001). It was concluded by the IPCS that for a total intake of 14 mg per day there is a clear excess risk of skeletal adverse effects and there is evidence in increased risk on the skeleton at total fluoride intakes above about 6 mg per day (IPCS, 2002).

3.3.3 Cancer

Studies from the exposed population, primarily from aluminium smelting, show an increase incidents of mortality, lung and bladder cancer. A number of epidemiological studies showing possible association between cancers and exposure to fluoride in drinking water. In spite of large number of studies conducted, there is no evidence to demonstrate association between the consumption of drinking water which has fluoride content and morbidity or mortality from cancer (USPHS, 1991; USNRC, 1993; WHO, 1996; IPCS, 2002).

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3.3.4 Other Possible Health Effects

A number of epidemiological studies have been carried out to examine the other possible adverse outcomes as a consequence of exposure to fluoride, either from drinking-water or other reasons. Studies on the association between exposure of mothers to fluoride in drinking-water and adverse pregnancy outcome have shown no increased risk of either spontaneous abortion or congenital malformations. No reasonable evidence of effects on the respiratory, haematopoietic, hepatic or renal systems have emerged from studies of occupationally exposed populations that could be attributed specifically to fluoride exposure. In addition,

such studies have failed to produce convincing evidence of genotoxic effects. The majority of fluoride is excreted via the kidneys (USNRC, 1993). Thus it is reasonable that those with impaired renal function might be at greater risk of fluoride toxicity than those without. In discussing this point, WHO (1996) concluded that the data were too limited to permit any quantitative evaluation of possible increased sensitivity due to impaired kidney function.

3.4 Impact of Fluoride on Soil

The fluoride concentration is commonly lower in soil and the concentration in the soil solution may be sufficient to induce adverse effects. Fluoride present in soil are related with soil colloid or clay fraction and its mobility in soil dependent on soil sorption capacity, varies with pH, types of sorbents present, and soil salinity. Retention of fluoride in soils because of clay and organic carbon content in the soil as well as the pH of the soil. In soils, fluoride is combined with aluminium or calcium and soils of silt and clay loam soils had higher fluoride content than sandy soil (Tylenda, 2011).

3.5 Impact of Fluoride on Animals

Fluoride will accumulate in tissues of animals that have high calcium contents, such as teeth and bones. It is generally conceded that some fluoride is beneficial for healthy animals may range between 80 and 200 mg/kg. Fluoride provided in forage, water or as mineral residues may result in accumulation of fluoride to more than 2000 mg/kg Animals that eat fluorine-containing plants may accumulate large amounts of fluorine in their bodies. Fluorine primarily accumulates in bones. Consequently, animals that are exposed to high concentrations of fluorine suffer from dental decay and bone degradation.

Chapter 4

MATERIALS AND METHODS

4. MATERIALS AND METHODS

This chapter presents the details of the study area, the procedure of sample collection, determination of fluoride concentration in the collected samples and deflouridation behaviour of selective reagents.

4.1 Study Area

Talcher coalfield has assumed great importance in the coal map of India and ranks first among the power grade coal deposits of the country. This coalfield lies about 105 km north – west of Cuttack. It constitutes the extreme south–eastern member of the Lower Gondwana basins within Mahanadi Valley Graben. It is connected with other Mahanadi Valley coalfields with narrow strips of Lower Gondwana strata (Chandra et al.) At present, there are 8 opencast projects (OCPs) and there underground mines operating in Talcher coalfields. These mines are

Opencast Mines

1. Ananata OCP
2. Jagannath COP
3. Bhubaneswari OCP
4. Bharatpur OCP
5. Lingraj OCP
6. Hingula OCP
7. Balram OCP
8. Kaniha OPC

The names of the different underground mines in Talcher are

1. Deulabeda Colliery
2. Talcher Colliery
3. Nandira Colliery

The Talcher Coalfields are provides raw material to Talcher Thermal Power Station (NTPC), NTPC Kaniha, National Aluminum Company Limited, and private washeries like Global

Coal Washeries and other private companies like APGENCO, Vishakhapatnam Steel, KPCL, RPTT etc. (Choudhury, 2012).

In order to study fluoride pollution, water and fly ash samples were collected from different location of Talcher Coalfields. The location of Talcher coalfield has been shown in Fig. 4.1. It is located between longitudes 84^0 09' – 85^o 33' and and latitude 20^0 50'-21^0 15' strike length of the coalfield in east-west direction is about 80 kms and the width in north south direction is about 26 Kms. Talcher Coalfield covers an area of 1813 sq. Km. The coal reserve in Orissa as on 1st April is estimated to be 75.799 billion tonne and percentage of total reserve of India is 24.72% second largest reserve in India after Jharkhand. The Talcher Coalfield has reserves of 50.968 billion tonnes as on 2015-2016 the highest in India. In 2016-17, MCL turned up to be the largest coal producing subsidiary of CIL and hence, was given the biggest target of 167 MT. The coal contains about 35 per cent of fixed carbon, 70 per cent volatile matter and 25 per cent ash content.

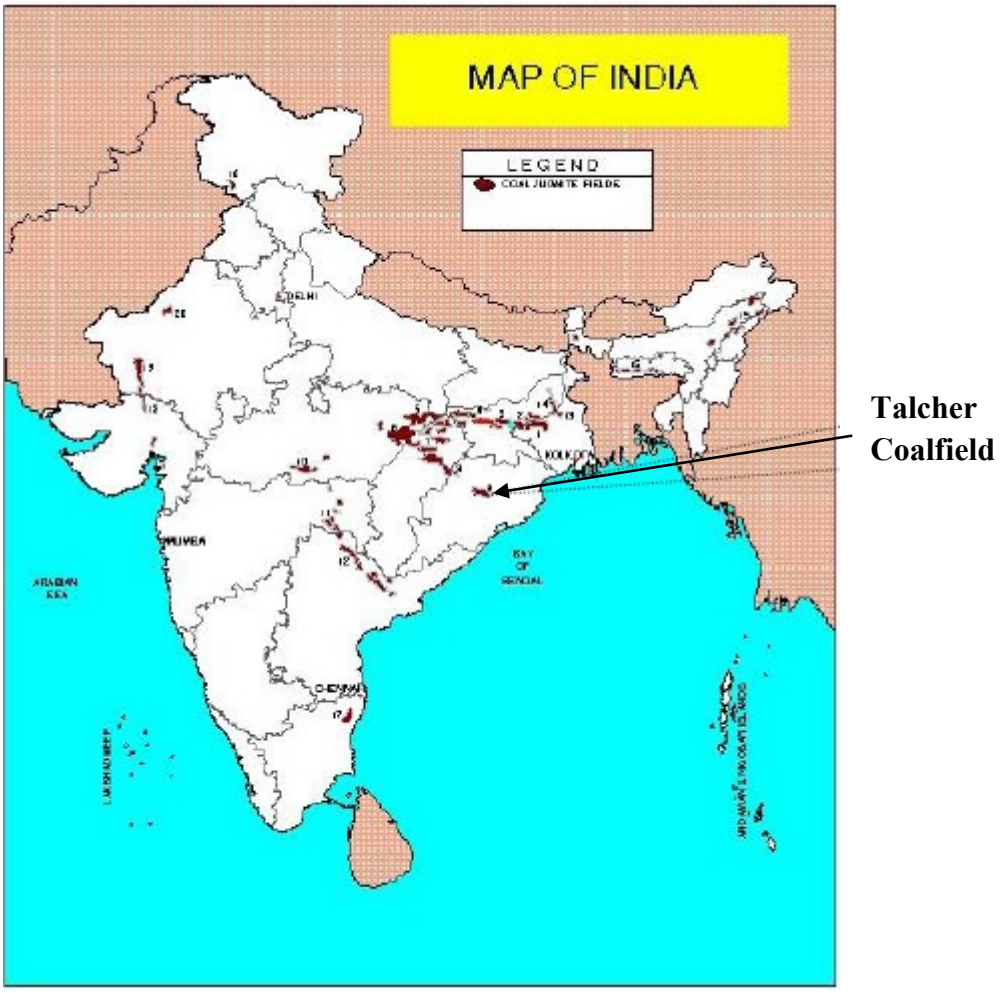

Fig 4.1: Geographical representation of Study Area

Topographically the coalfield can be divided in two parts - eastern part and the western part. The eastern part largely covered by Barakar Formation (or Lower Kamthi Formation), is slightly undulating with an average elevation of around 150m above MSL. The western part comprises largely of steeply sloping Kamthi hillocks. Minimum and maximum elevation from MSL is 60m and 567m respectively for the coalfield. The terrain is undulating and accommodates large number of Page 4 of 382 villages and fertile lands. The soil in this area varies from rich loams to the gravelly detritus of the hill slopes. The coalfield is drained by the Brahmani River flowing along eastern fringe of the coalfield. Singhadajhor, Nandira and Tikra, Aunli are some of the important tributaries of the Bramhani River.

4.2 Sample Collection

Water and fly ash samples were collected for the study. Water samples were collected from three locations of Jagannth and Balanda colliery, viz central and waste sump of Jagannath Colliery and decanted water of Balanda abandoned pit. It may be noted that the flyash filling is being done in central sump whereas the natural runoff is stored in west sump. Water samples were collected in 10 litre plastic containers. Fly ash sample was collected from the abandoned quarries of Balanda opencast project (Fig. 4.3). It may be noted that the coal of the Balanda open cast project have been completely excavated and the mine is filled with flyash which is transported through pipeline from the nearby Talcher thermal power plant belonging to NTPC (National Thermal Power Corporation).

Fig. 4.2: Sampling Locations shown on Google map

Fig 4.3: Collection of Fly ash Sample from Balanda OCP

4.3 Determination of Fluoride Content of Water Samples

The water samples in the containers were shaken well. Then number of beakers was taken and 100 mL of sample solutions were added into each beaker. Then 10 ml of sample from each beaker were taken in as many small beakers and 1 ml of TISAB III were added into each of them in order to maintain 10:1 sample and TISAB III ratio. Finally readings were taken from Orion Fluoride Ion meter.

Procedure

1. First connect the electrode to the meter. Then set the meter to ISE mode.
2. The electrode was thoroughly rinsed with distilled water and flushed with filling solution by pressing cap of the electrode followed by refilling with fresh filling solution.
3. Different standard fluoride solution such as 1 ppm, 10 ppm and 100ppm were prepared to calibrate the ion meter. After calibration the slope should be in the range of -54 to -60 millivolt range.
4. Afterwards the amount of fluoride was measured in ppm by putting the fluoride ion selective electrode into the sample solution.

Fig 4.4 : TISAB III, Electrode and Ion Selective Electrode meter.

Result of the fluoride concentration in Ash Pond, Central Sump and West Sump and has been presente in Table 4.1 . The results showed that there is high fluoride present in the waters of ash pond and central sump compared to west sump. Therefore, further analysis were carried out for the waters of ash pond and central sump only.

Table 4.1: Results of Fluoride Concentration and pH Value

Samples	Fluoride (in ppm)	pH
Ash Pond	8.1	2.88
Central Sump	9.8	5.63
West Sump	0.39	3.37

Precautions

- Do not drink, smell while using TISABIII use hand gloves, safety glasses for eyes, masks.
- Immediately wash the hand and face with soap and water after using TISABIII.
- The tip of the electrode is very sensitive so avoid touching it with hands, the electrode should be cleaned with the help of distilled water and tissue papers after each and every Fluoride measurement.
- Make sure that the tip of the electrode is completely dipped in the sample which is taken in a beaker and also see that the tip should not touch the base of the beaker.

4.4 Leaching of Fluoride from Fly ash

Leaching test was performed following solid waste-extraction procedure for leaching toxicity, 2010. In this method 10g of sample was taken into a 200 ml flask and 1ml of leaching agent namely distilled water was added to have water to solid ratio of 10:1. The sample solution is kept in a orbital shaking incubator at 30 rpm for 24 hour at room temperature. Then the sample solution was filtered using 0.45-µm membrane filter paper. Finally the fluoride concentration was measured with the help of Ion meter. pH was analyzed immediately with pH meter

Table 4.2: Fluoride Concentration and pH value in Fly ash Leachate

Sample	F^- (in ppm)	pH
fly ash with distilled water	1.8	5.79
fly ash with acetic acid	1.2	5.62

4.5 Assessment of Defluoridation behaviour using different Reagents

The defluoridation techniques are (1) coagulation, (2) adsorption (including ion exchange), (3) electrochemical methods, and (4) membrane processes.

Coagulation:

The following steps were carried out for removal of fluoride by coagulation: (i) neutralization of negatively charged colloids by cationic hydrolysis products and (ii) incorporation of impurities into an amorphous precipitate of metal hydroxide. The two mechanisms depend on

many factors like pH and coagulant dosage. Coagulation by defluoridation technique includes (a) precipitation of fluoride by a proper reagent through chemical reactions; (b) co precipitation of fluoride, which embraces simultaneous precipitation by a macro-component from the similar solution by the development of mixed crystals, by multiple contrivances such as adsorption, occlusion, or mechanical entrapment (Gupta and Ayoob, 2016).

Adsorption:

Adsorption is the interface amalgamation of substances on a surface. Adsorbate is the material that is being absorbed, and the phase that adsorbs is called adsorbent. "Physisorption," or "chemisorption," are the two types of adsorption. Physisorption at low temperatures is noteworthy and low energy of adsorption is established, which specifies that the adsorbate is seized loosely with the adsorbent. If the adsorbate develops a chemical reaction with the adsorbent, the process may be stated as chemisorption. The "ion exchange" may be treated as an "exchange adsorption," where "ions of one substance accrue at the surface as a result of electrostatic attraction to charged sites at the surface. Ion exchange is one of the most recurrently used methods for defluoridation. The ability of being adsorbed cost of the adsorbent and skill for reuse and reinforcement are some of the parameters that define the selection of an adsorbent.

In the present study coagulation technique using alum, and adsorption of fluoride using activated carbon has been presented (Gupta and Ayoob, 2016).

Electrochemical Methods:- The electrochemical method is of two types (a) electrocoagulation (b) electrosorption. Electrocoagulation (EC) comprises a procedure which is electrolytic in nature for producing a coagulant through the oxidation of proper anodic materials. The coagulant ions unrestricted react with the ions (targeted to be removed), originating a normal coagulation process. Aluminum and iron are used as sacrificial electrodes. The proficiency of this process is nearly 100% at optimum pH of 5–7.6. With increase in temperature the efficiency reduces due to fluoride desorption from aluminum hydroxide by obliteration of fluoro-aluminum complexes. Issues such as interference from other anions present in water due to the competition effect may reduce the efficiency of the EC process. Steady replacement of sacrificial electrodes due to continuous dissolution into solution and high consumption of electric power during operation may be treated as limitation of the process (Gupta and Ayoob, 2016).

Electrosorptive method is used to upsurge the sorption capacity of the conventional systems. The efficiency of the alumina bed got expressively better by means of a new activation technique by the claim of an electric field. The technique shows more efficiency than the conventional activation techniques. The regeneration of an adsorbent plays a crucial role in its selection, economical evaluation, and field application. Any reduction in the cost of the regeneration will significantly enhance the efficiency of the adsorbent bed and the method. The amount of water necessary for the regeneration of the saturated bed is very minimal compared with conventional techniques (Gupta and Ayoob, 2016).

Membrane Processes:

Membrane is a selective barrier controlling material transport between two adjacent phases. A widespread variety of technical applications are likely by varying or fluctuating the membrane structure, cross section, and shape. The difference in chemical potential because of concentration or pressure gradient through the membrane (or by an electric field) acts as the force which drives passive transport in membrane separations. (Gupta and Ayoob,2016).

The applications of membrane processes in water treatment is further advantageous, as many of the complications found in precipitation, coagulation, or adsorption can be circumvented or lessened.The basic principles governing the membrane-based processes are Reverse osmosis, Nano filtration and electro dialysis (Gupta and Ayoob, 2016).

4.5.1 Alum

The metal gets hydrated when Aluminium salt is dissolved in water and form an aquo metal ion AL $(H_2O)_6^{3+}$ which on further hydrolysis forms a series of mononuclesr, dinuclear, and possibly polynuclear hydroxo complexes. At the interfaces Hydroxometal get adsorbed and is responsible for destabilization of colloids in water that is treated with aluminium salts through charge neutralization. The mechanism of fluoride removal due to alum addition may be due to

- Forming a precipitate when co precipitates of fluoride and hydroxide (OH).
- Adsorption or ligand exchange

Removal of fluoride using alum depends on the pH, alkalinity, the coexisting anions and other characteristics of solution. Limitation of alum treatment is the increase in aluminium and sulphate concentration into treated water. For defluoridation by coagulation the pH should be in the range of 5.5-6.5. (Mjengera & Mkongo, 2003; Fan et al., 2003; Sujana et al., 1998).

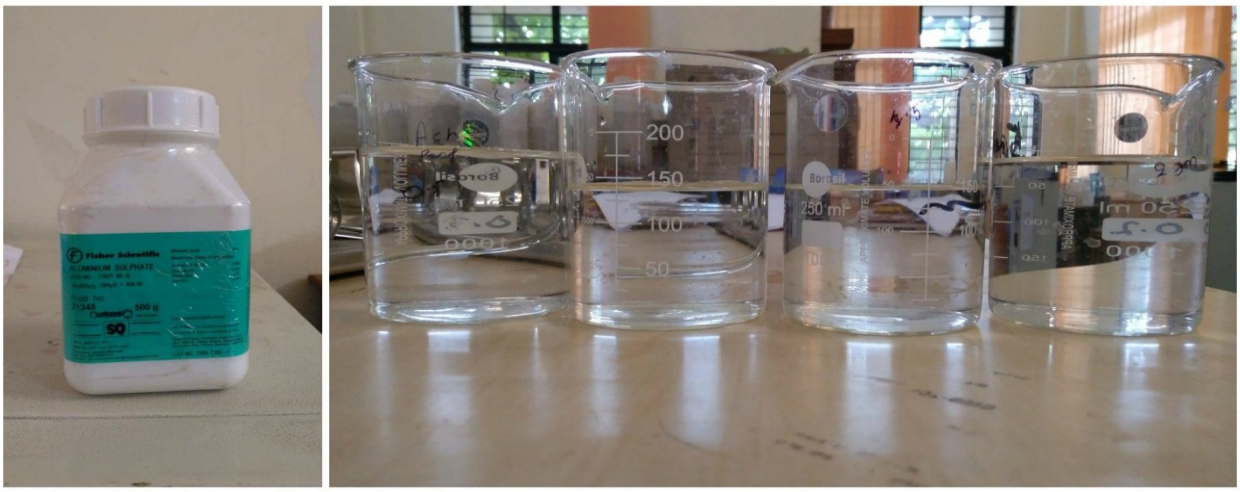

Fig 4.5: Photographic view of samples preparation at different doses using Alum for Ash pond Water

Table 4.3: Variation of Fluoride Concentration, pH and Turbidity with Time at 0.3g of Alum in Ash Pond Water

Duration (in Hrs.)	Alum (in gm)	Fluoride Conc. after Treatment (ppm)	pH Value	Turbidity (NTU)
0	0	8.2	5.70	87.0
1	0.3	0	1.60	78.0
2	0.3	0	1.57	72.0
3	0.3	0.29	1.55	67.1
4	0.3	0.28	1.55	66.2
24	0.3	0	1.49	-

Table 4.4: Variation of Fluoride concentration, pH and Turbidity with time at 0.2g of Alum in Ash Pond Water

Duration (in Hrs.)	Alum (in gm)	Fluoride Conc. after Treatment (ppm)	pH Value	Turbidity (NTU)
0	0	8.2	5.98	87.0
1	0.2	0.22	1.66	59.9
2	0.2	0.17	1.63	49.7
3	0.2	0.15	1.62	48.2
4	0.2	0.13	1.58	46.1
24	0.2	0.11	1.56	-

Table 4.5: Variation of Fluoride Concentration, pH and Turbidity with Time at 0.1 g of Alum in Ash Pond Water

Duration (in Hrs.)	Alum (in gm)	Fluoride Conc. after Treatment (ppm)	pH Value	Turbidity (NTU)
0	0	8.2	6.20	87.0
1	0.1	0.53	1.72	58.7
2	0.1	0.51	1.71	55.6
3	0.1	0.47	1.68	54.1
4	0.1	0.46	1.66	51.1
24	0.1	0.45	1.64	

Table 4.6: Variation of Fluoride Concentration, pH and Turbidity with time at 0.5g of Alum for Central Sump Water

Duration (in Hrs.)	Alum (in gm)	Fluoride Conc. after Treatment (ppm)	pH Value	Turbidity (NTU)
0	0	9.8	6.33	7
2	0.5	0.93	1.78	0.44
4	0.5	0.80	1.79	0.35
6	0.5	0.90	1.75	0.34
8	0.5	0.72	1.84	0.60
10	0.5	0.72	1.80	
12	0.5	0.70	1.78	
14	0.5	0.68	1.77	
24	0.5	0.65	1.72	

Table 4.7: Variation of Fluoride concentration, pH and Turbidity (NTU) with time at 1.0g of Alum for Central Sump Water

Duration (in Hrs.)	Alum (in gm)	Fluoride Conc. after Treatment (ppm)	pH Value	Turbidity (NTU)
0	0	9.8	6.33	7
2	1.0	0.058	1.65	0.50
4	1.0	0.057	1.80	0.30
6	1.0	0.055	1.74	0.32
8	1.0	0.056	1.72	0.39
10	1.0	0.054	1.70	-
12	1.0	0.050	1.71	-
14	1.0	0.053	1.69	-
24	1.0	0.052	1.68	-

Table 4.8: Variation of Fluoride Concentration, pH and Turbidity with Time at 1.5g of Alum for Central Sump Water

Duration (in Hrs.)	Alum (in gm)	Fluoride Conc. after Treatment (ppm)	pH Value	Turbidity (NTU)
0	0	9.8	6.33	7
2	1.5	0.030	1.66	0.52
4	1.5	0.033	1.72	0.60
6	1.5	0.024	1.73	0.62
8	1.5	0.030	1.68	0.89
10	1.5	0.028	1.68	-
12	1.5	0.029	1.66	-
14	1.5	0.030	1.65	-
24	1.5	0.028	1..63	-

Table 4.9: Variation of Fluoride Concentration, pH and Turbidity with Time at 2.0g of Alum for Central Sump Water

Duration (in Hrs.)	Alum (in gm)	Fluoride Conc. after Treatment (ppm)	pH Value	Turbidity (NTU)
0	0	9.8	6.33	7
2	2.0	0.018	1.62	0.46
4	2.0	0.019	1.63	0.70
6	2.0	0.016	1.66	0.83
8	2.0	0.019	1.64	0.73
10	2.0	0.018	1.62	-
12	2.0	0.017	1.60	-
14	2.0	0.011	1.58	-
24	2.0	0.012	1.57	-

4.5.2 Alum and Lime (Nalgonda Technique)

A mechanism in Nalgonda technique such as mixing, flocculation, sedimentation, filtration and disinfection when adding alum, lime and bleaching powder in a raw water. $1/20^{th}$ to $1/25^{th}$ that of filtered alum is used as dose of lime. For disinfection, bleaching powder is added at the rate of 3 mg/l. In Nalgonda technique, a coagulant is mixed with alum followed by charge neutralization. It is a generally used for community application for serving around 200 people. Low cost and ease handling are its merits. Limitation of this technique include medium efficiency, high alum dose, higher pH content, and salinity (Suneetha, 2008). The photographic view of the experimental et up and process chemicals has been presented in Fig. 4.6. The variation of fluoride concentration in the Ash pond and central sump water with addition of 0.3 gm, 0.2 gm and 0.1 gm of alum has been presented in Tables 4.10 to 4.12 respectively.

Fig 4.6: Photographic View of Samples Preparation at Different Doses using Alum, Lime and Bleaching Powder

Table 4.10: Variation of Fluoride Concentration and pH with Time at 0.3g of Alum for Central Sump and Ash Pond Water using Nalgonda Technique

Duration (Hrs.)	Alum (gm)	Lime (gm)	Bleaching Powder (img)	Central Sump		Ash Pond	
				Fluoride (ppm)	pH Value	Fluoride (ppm)	pH Value
0	0	0	0	9.8	6.21	8.2	6.12
1	0.3	0.01	3	0	3.52	0	3.69
2	0.3	0.01	3	0	2.93	0.19	3.60
3	0.3	0.01	3	0	2.65	0	3.62
4	0.3	0.01	3	0.18	3.10	0	3.62
24	0.3	0.01	3	0	3.95	0	4.03

Table 4.11: Variation of Fluoride Concentration and pH with Time at 0.2g of Alum for Central Sump and Ash Pond Water using Nalgonda Technique

Duration (Hrs.)	Alum (gm)	Lime (gm)	Bleaching Powder (img)	Central Sump		Ash Pond	
				Fluoride (ppm)	pH Value	Fluoride (ppm)	pH Value
0	0	0	0	9.8	5.58	8.2	5.95
1	0.2	0.008	3	1.2	3.45	0.28	3.66
2	0.2	0.008	3	1.2	3.42	1.8	3.61
3	0.2	0.008	3	1.3	3.23	0.47	3.59
4	0.2	0.008	3	1.6	2.85	0.76	3.54
24	0.2	0.008	3	2.2	3.95	1.5	4.08

Table 4.12: Variation of Fluoride Concentration and pH with Time at 0.1g of Alum for Central Sump and Ash Pond Water using Nalgonda Technique

Duration (Hrs.)	Alum (gm)	Lime (gm)	Bleaching Powder (img)	Central Sump		Ash Pond	
				Fluoride (ppm)	pH Value	Fluoride (ppm)	pH Value
0	0	0	0	9.8	5.60	8.2	5.98
1	0.1	0.004	3	2.0	3.67	3.1	3.86
2	0.1	0.004	3	2.3	3.47	3.0	3.73
3	0.1	0.004	3	2.6	3.27	3.0	3.77
4	0.1	0.004	3	2.1	2.95	2.9	3.69
24	0.1	0.004	3	2.8	3.60	3.1	4.20

4.5.3 Activated Carbon

An attempt was made to study the fluoride removal behaviour using activated carbon using coal. Activated carbon is a non-graphitic form of carbon, which is produced by activation of any carbonaceous material such as jute sticks, coconut shells, bamboo, wood chips, sawdust, coal, lignite, paddy husk etc. Without addition of chemicals or bonding agents, the charcoal powder is completely natural and odour free. Activated carbon is prepared in furnace at 600 °C for 3 hour. The pH of the water sample depends on type of coal (Regassa et al., 2016, Emmanuel et al., 2008). The photographic view of preparation of activated carbon in the laboratory is presented in Fig. 4.7. The variation of fluoride concentration in the waters of central sump and ash pond using 1.2gm, 1gm and 0.8gm of activated carbon has been presented in Figures 4.13 to 4.15 respectively.

Fig. 4.7: Photographic View of Preparation of Activated Coal in the Laboratory

Table 4.13: Variation of Fluoride Concentration and pH at 1.2g of Activated Carbon for Central Sump and Ash Pond Water

Duration (Hrs.)	Activated Coal (gm)	Nitric Acid (ml)	Central Sump		Ash Pond	
			Fluoride (ppm)	pH Value	Fluoride (ppm)	pH Value
0	0	0	9.8	3.80	8.2	3.70
1	1.2	10	0.1	1.62	0.08	1.88
2	1.2	10	0.1	1.61	0.07	1.82
3	1.2	10	0.08	1.59	0.07	1.79
4	1.2	10	0.06	1.55	0.06	1.75
24	1.2	10	0.02	1.54	0.05	1.68

Table 4.14: Variation of Fluoride Concentration and pH at 1.0g of Activated Carbon for Central Sump and Ash Pond Water

Duration (Hrs.)	Activated Coal (gm)	Nitric Acid (ml)	Central Sump		Ash Pond	
			Fluoride (ppm)	pH Value	Fluoride (ppm)	pH Value
0	0	0	9.8	3.66	8.2	3.63
1	1.0	10	0.22	1.45	0.13	1.67
2	1.0	10	0.20	1.42	0.12	1.66
3	1.0	10	0.18	1.41	0.11	1.63
4	1.0	10	0.17	1.39	0.09	1.61
24	1.0	10	0.15	1.37	0.07	1.57

Table 4.15: Variation of Fluoride Concentration and pH at 0.8g of Activated Carbon for Central Sump and Ash Pond Water

Duration (Hrs.)	Activated Coal (gm)	Nitric Acid (ml)	Central Sump		Ash Pond	
			Fluoride (ppm)	pH Value	Fluoride (ppm)	pH Value
0	0	0	9.8	3.62	8.2	3.30
1	0.8	10	0.29	1.32	0.21	1.39
2	0.8	10	0.25	1.29	0.20	1.38
3	0.8	10	0.24	1.28	0.19	1.37
4	0.8	10	0.22	1.27	0.18	1.29
24	0.8	10	0.20	1.22	0.15	1.27

Chapter 5

DISCUSSION AND CONCLUSION

5. DISCUSSION AND CONCLUSION

5.1 DISCUSSION

Recently, there have been reports of increase in the concentration of fluoride in both surface and ground waters in and around Talcher Coalfield. Therefore, Talcher coalfield was chosen as a case study for the assessment and control of fluoride. The untreated waste water contaminated with fluoride discharged from industrial units are either allowed to accumulate in the lagoon or discharged to the river without adequate treatment. The water from the mining region mix with the Nandira and Bangaru nallah, finally terminating with Brahmani river. The ground water also gets contaminated by percolation through the soil. A large number of villagers have reported fluoride induced symptoms like pain in the lower leg. The domestic animals like castles have shown bone related problems in this region. While Talcher is among the worst affected, there are other districts where the problem has assumed serious proportions.

In order to increase the utilization of fly ash, the State Pollution Control Board has stressed upon the need of filling the abandoned mine voids with fly ash. Accordingly, the fly ash generated from TTPS (NTPC), Bhusan Steel Ltd, Bhusan Energy Ltd. and Nava Bharat Ventures Ltd. Are being disposed in abandoned mine voids. The TTPS conveys its ash slurry through pipeline upto the voids and other plants transport ash in moist condition. Laying of pipeline for ash disposal by NALCO (CPP) in abandoned mine pits are under progress. As the fly ash that is being released from the power plant gets percolated into water without being treated so there is a probability that high content of beyond the permissible limit as specified by the WHO guidelines may leaching, causing contamination of ground water.

In this study, removal of fluoride by coagulation process using Alum and Nalgonda technique; and adsorption by activated carbon was studied. The effect of each adsorbent has been examined and discussed. The effect of the coagulants on turbidity and pH were also studied. The variation of fluoride concentration, turbidity and pH values for different doses of alum has been presented in Fig. 5.1 to 5.3. Similarly, the variation of fluoride concentration, turbidity and pH values for different doses of alum has been presented in Fig. 5.4 to 5.6. I may be noted that the initial fluoride concentration in ash pond and central sump are 8.2 ppm and 9.8 ppm respectively.

Treatment with Alum

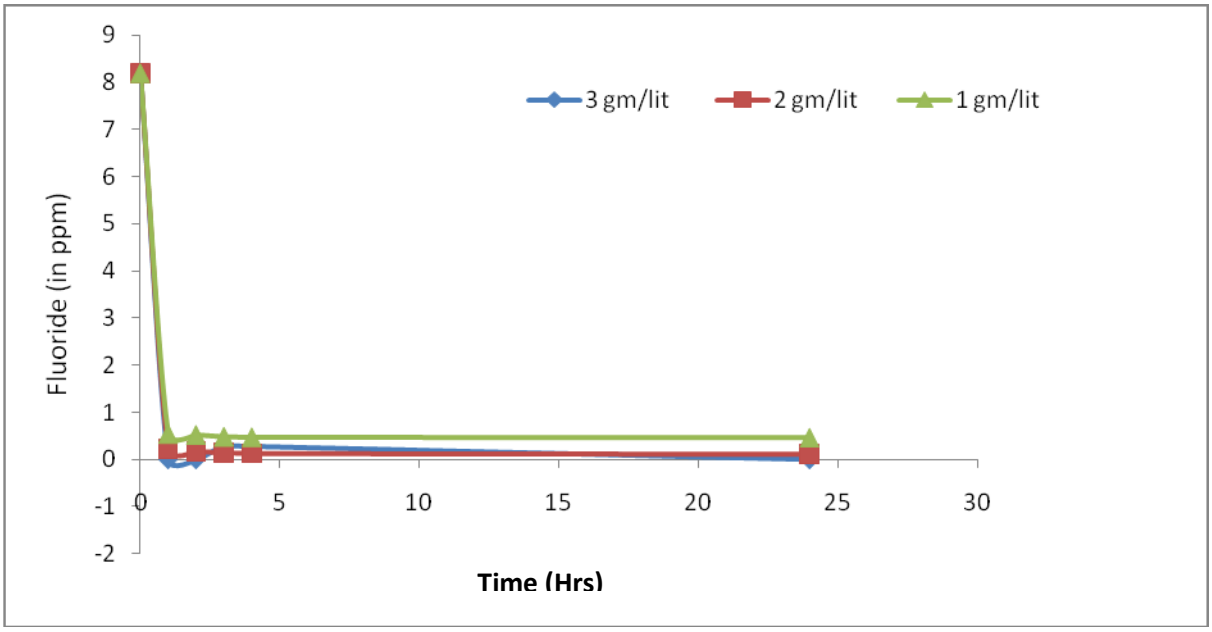

Fig 5.1: Variation of Fluoride Concentration with Time at Various Doses of Alum for Ash Pond Water

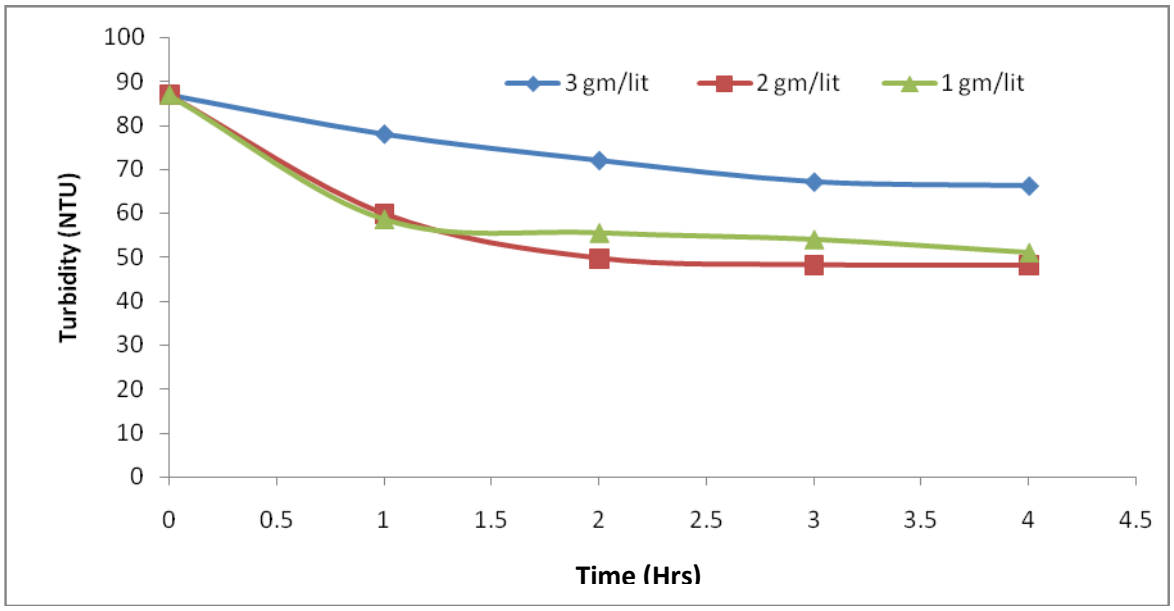

Fig 5.2: Variation of Turbidity with Time at Various Doses of Alum for Ash Pond Water

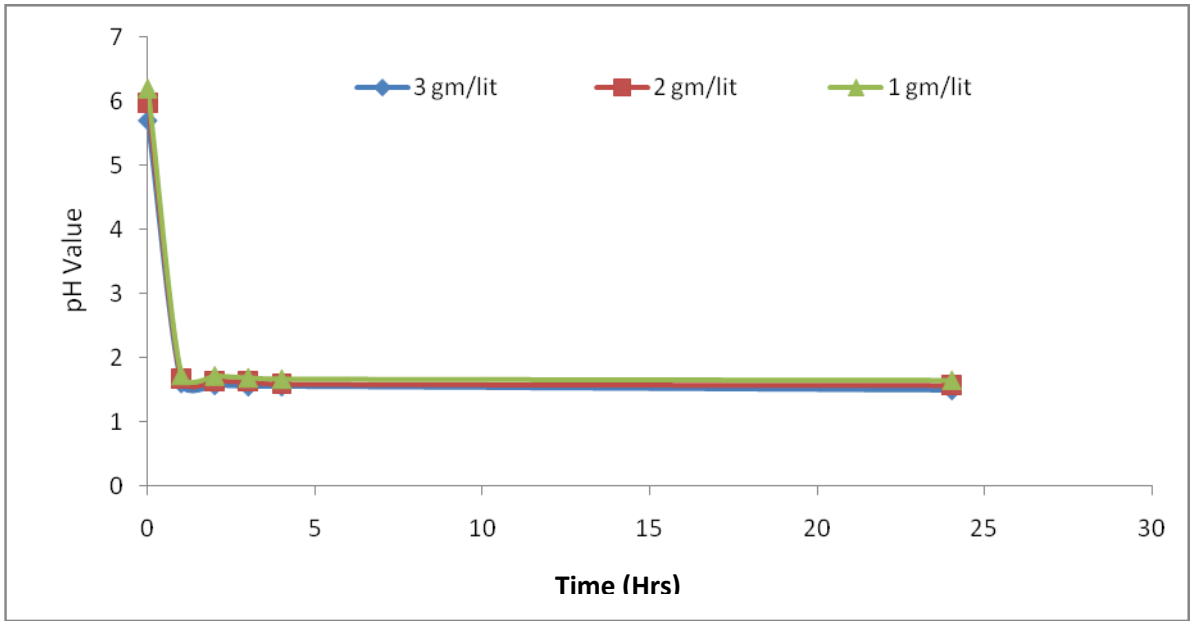

Fig. 5.3: Variation of pH with Time at Various Doses of Alum for Ash Pond Water

It may be noticed from Table 4.3 to 4.5 and Figure 51. To 5.3 that 100% fluoride removal was observed in the ash pond using 0.3gm/l of alum after 1 hour of treatment. However, it increased to 0.29 after three hours, which may be due to instrument errors. There was not much impact on the turbidity values which decreased slightly from 87 to 78 after 1 hours of treatment and subsequently to 66 after 4 hours. The pH vale decreased drastically from 5.7 to 1.6, making the water highly acidic.

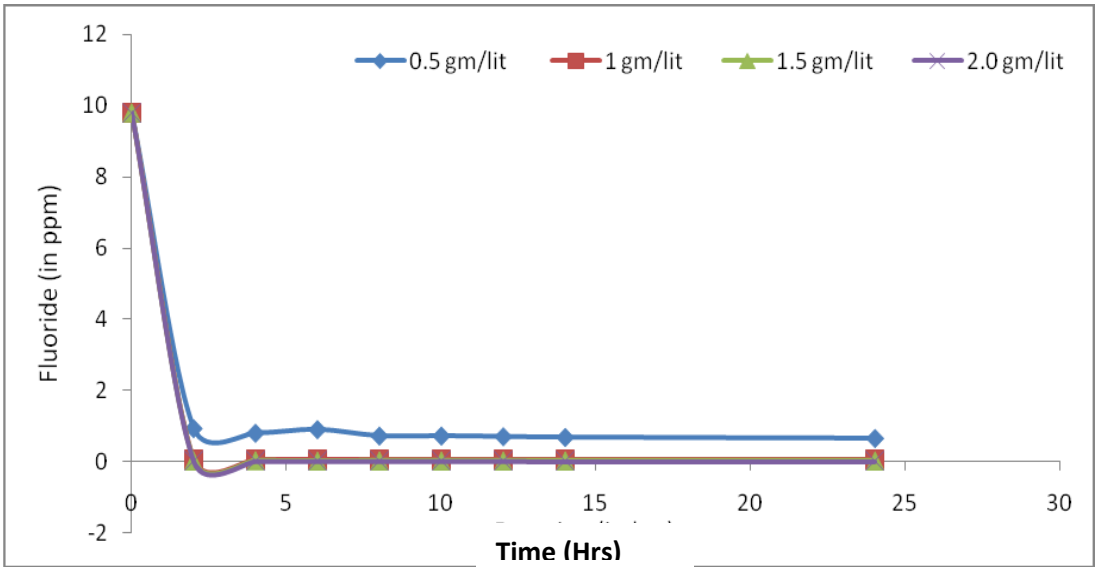

Fig. 5.4: Variation of Fluoride Concentration with Time at Various Doses of Alum for Central Sump Water

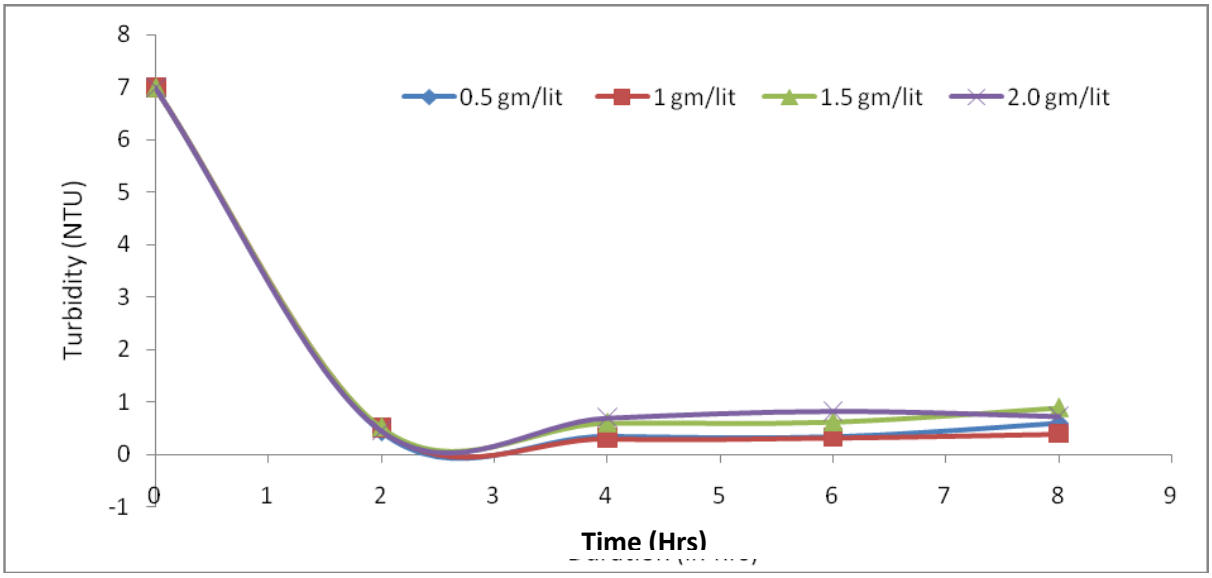

Fig. 5.5: Variation of Turbidity with Time at Various Doses of Alum for Central Sump Water

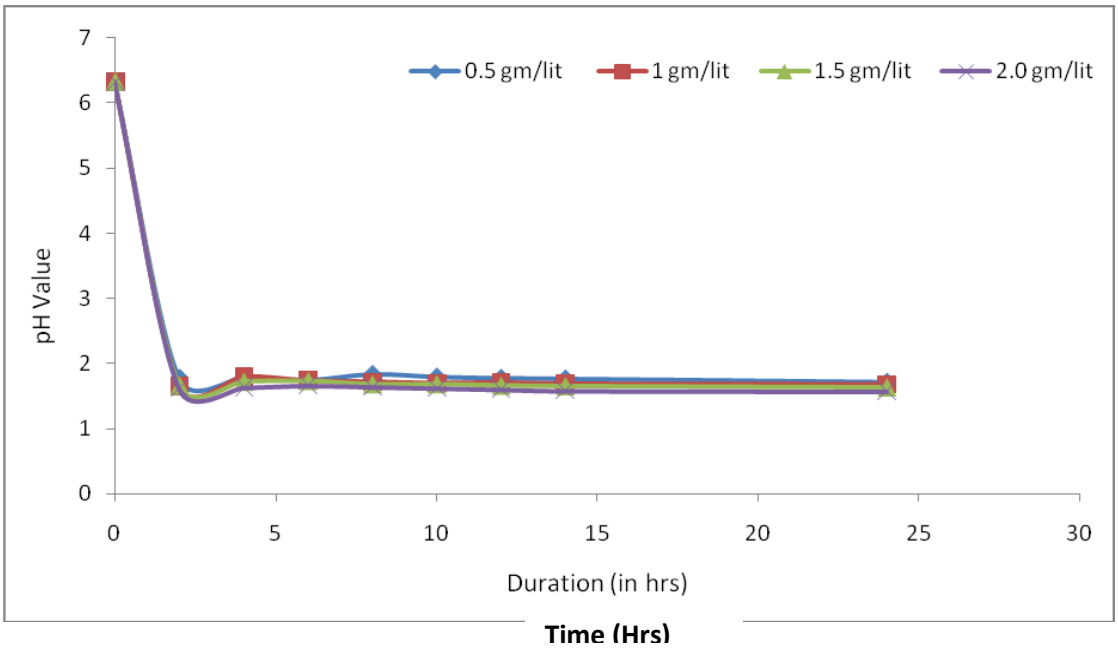

Fig. 5.6: Variation of pH with Time at Various Doses of Alum for Central Sump Water

For the central sump, the experiments started with a dose of 0.5g/l of alum, and the dose was increased in increments of 0.5gm/l till 2 mg/l, where optimum fluoride removal was obtained. It may be noticed from Table 4.6 to 4.9 and Figure 5.4 to 5.6 that the fluoride concentration came below the permissible limits after 2 hours of treatment with 1 gm/l of alum. Therefore 1mg/ l may be considered the optimum dose. The turbidity values reduced from 7 to 0.5 and

the pH value from 6.33 to 1.66 after 2 hours of treatment. Thus it may be concluded that by using alum more than 99% removal of fluoride takes place at pH in the range of 5.5 to 6.5.

Nalgonda Technique

In Nalgonda technique alum, lime and bleaching powder ws mixed in different proportions as mentions ins section 4.5.2. The variation in fluoride concentration in the waters of ash pond and central sump has been presented in Figure 5.7 and 5.8, and pH valued have been presented i9n 5.9 and 5.10 respectively.

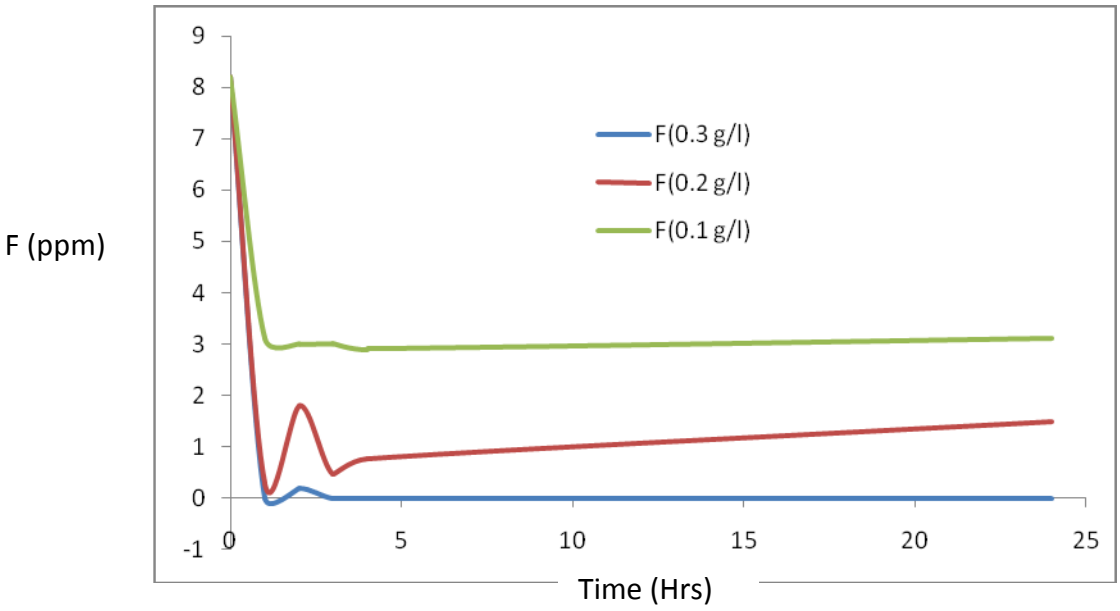

Fig 5.7: Variation of Fluoride Concentration with Time for Ash Pond Water

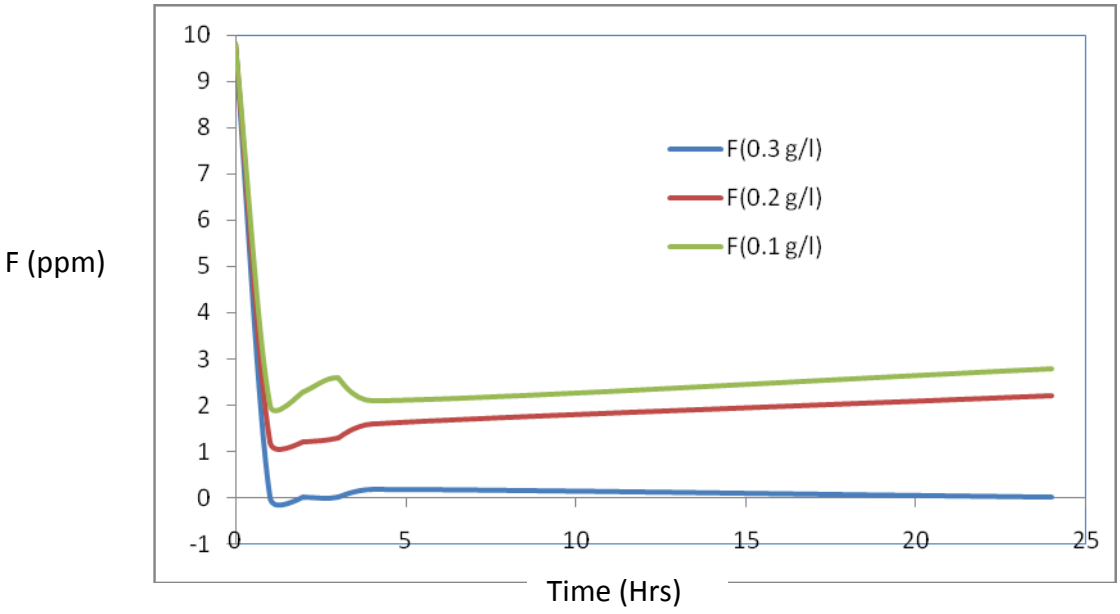

Fig 5.8: Variation of Fluoride Concentration with Time for Central Sump Water

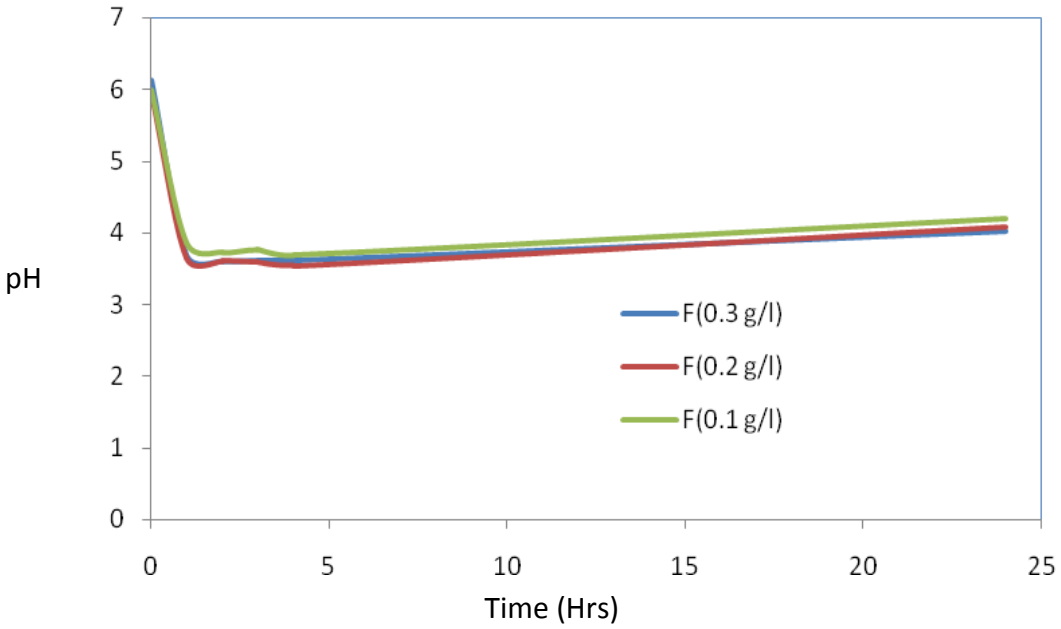

Fig 5.9: Variation of pH with time for Ash Pond Water

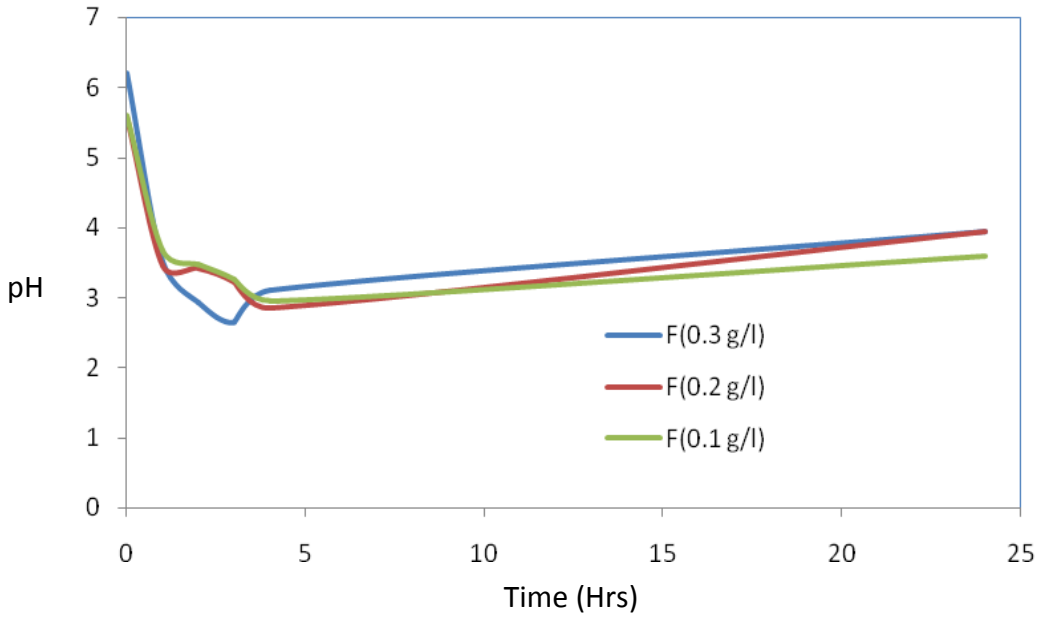

Fig 5.10: Variation of pH with Time for Central Sump Water

It may be observed from Fig5.7 and 5.8 and Tables 4.10 to 4.12 that with addition of 0.3 g/l of alum, 0.001 gm of lime and 3 gm/l of bleaching powder, 100% removal of fluoride can be carried from both the ash pond and central sump water after one hour. However, the pH value reduces to 3.69 and 3.52 respectively.

Activated Carbon

Activated carbon is known to a very good absorbent for several contaminants present in water. Therefore an attempt was made to remove the fluoride using activated carbon using 0.8gm, 1gm and 1.2 gm of activated carbon. The variation in fluoride concentration using activated carbon has been presented in Figures 5.11 and 5.12, and the variation in pH has been presented in figure 5.13 and 5.14 respectively.

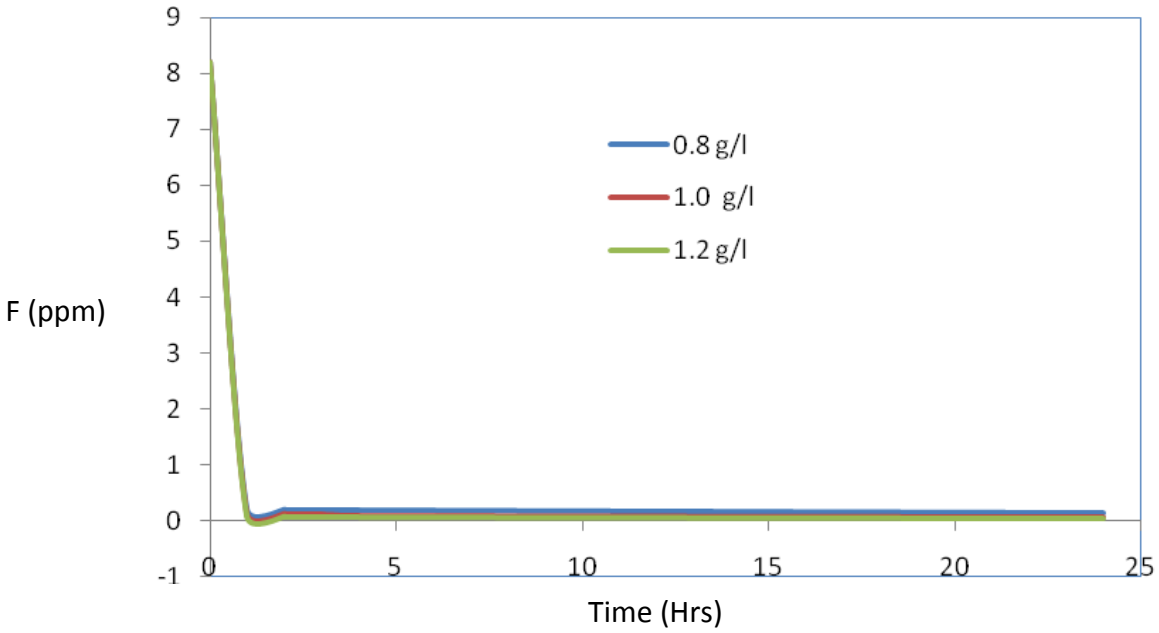

Fig. 5.11: Variation in Fluoride Concentration with Time at Different Doses of Activated Carbon for Ash Pond Water

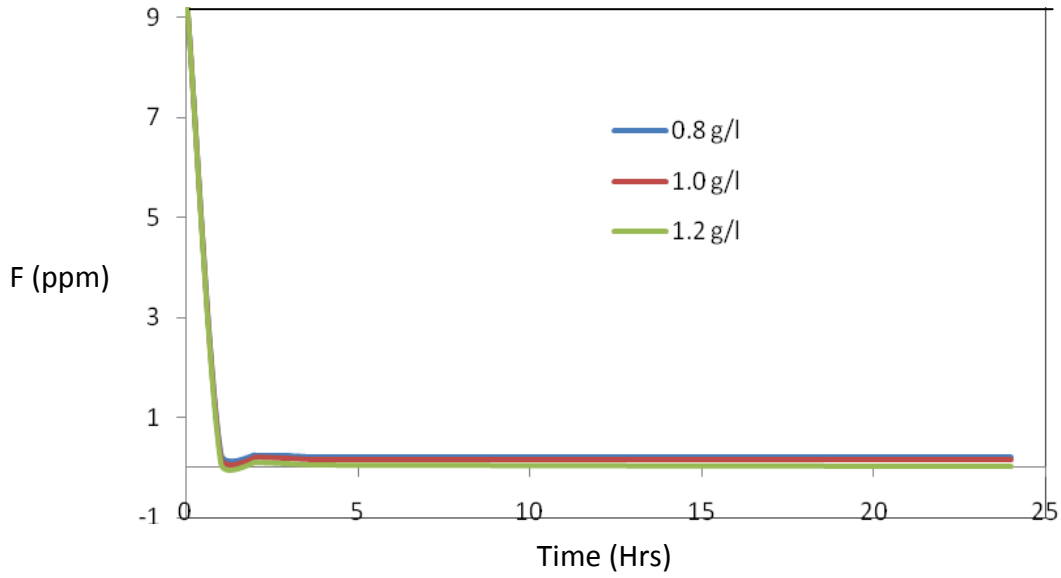

Fig. 5.12: Variation in Fluoride Concentration with Time at Different Doses of Activated Carbon for Central Sump Water

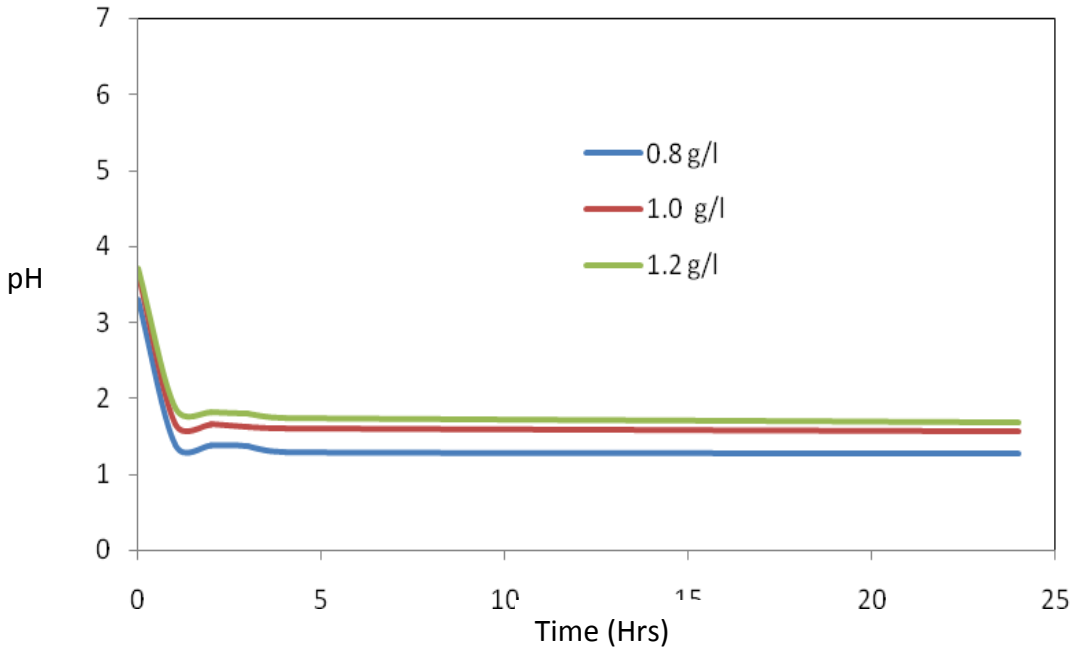

Fig. 5.13: Variation in pH with Time at Different Doses of Activated Carbon for Ash Pond Water

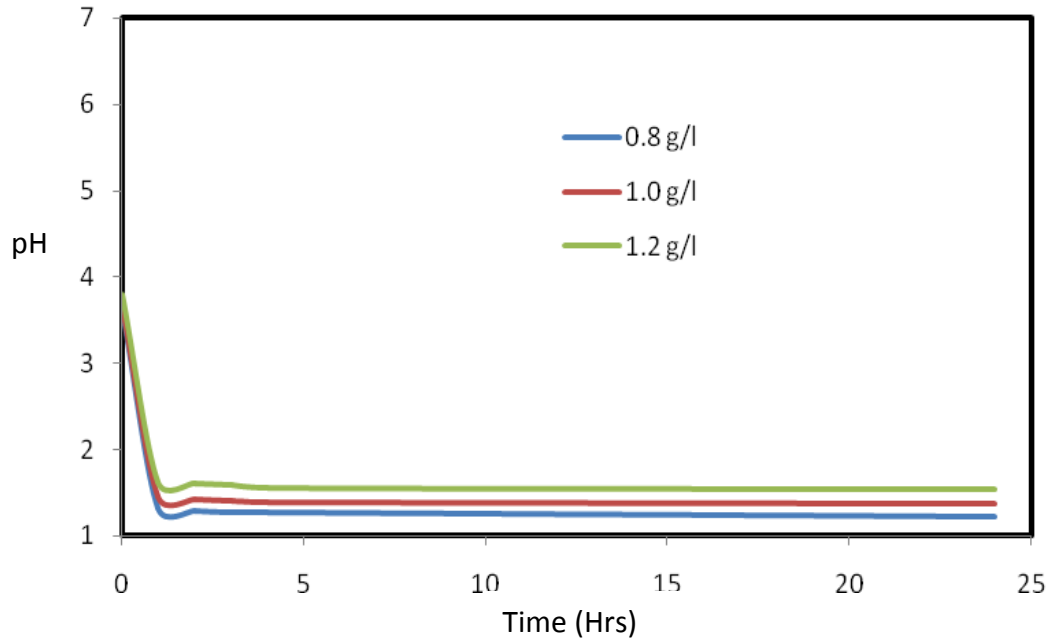

Fig. 5.14: Variation in pH with Time at Different Doses of Activated Carbon for Central Sump Water

It may be seen from Figure 5.11 and 5.12 that 0.8gm/ l of activated carbon the fluoride concentration comes below the permissible limit after 1 hour of treatment. It reduces slightly there after, so much so that after 24 hours the fluoride concentration has been found to be 0.15 gm/l and 0.20 gm/l in the waters of the ash pond and central sump respectively. The pH values in both the cases reduces 1.27 and 1.22 from 3.30 and 3.62 respectively.

5.2 Conclusion

Talcher coalfield belonging to Mahandai Coalfields Limited which is a subsidiary of the public sector enterprise Coal India Ltd.. It is one of major coalfields in our country. Recently, there have been reports of health hazards due to fluoride contamination among human being and animals in this region. Therefore, an attempt has been made in this study to asses the fluoride concentration in some selected areas of Talcher coalfield. Attempt have also been made to study the behaviour of fluoride removal using, two different methods namely coagulation using alum and Nalgonda technique; and adsorption using activated carbon were carried out. Earlier researchers have found that fluoride present in wastewater can be removed by using alum; which has a high efficiency of removal. The pH should be in the range of 5.5-6.5 for the maximum efficiency of removal of fluoride. It was found that 100% of fluoride can be removed with 0.3gm/l of fluoride. In order to reduce the cost, the treatment can also be carried out with 0.1 gm/l of alum, since the fluoride concentration comes below the permissible limit after 1 hour of treatment.

Nalgonda technique is a simple and economical method for fluoride removal. It is addition of alum, lime and bleaching powder followed by rapid mixing, flocculation, filtration and disinfection. Aluminium is added to the sample and it is responsible for removing fluoride. Increase in alum when fluoride is increase. $1/20^{th}$ to $1/25^{th}$ of that of the dose of the alum is the dose of lime. Bleaching powder is added at the rate of 3 mg/l for disinfection. It is preferred over the rest because of its low price and ease with which it is handledIn teh present case, it was seen that with addition of 0.3 g/l of alum, 0.001 gm of lime and 3 gm/l of bleaching powder, 100% removal of fluoride can be carried from both the ash pond and central sump water after one hour.

Activated carbon is a cost effective material, and is being used for widespread application including removal of different harmful contaminants present in water. It was seen that with the addition of 0.8g/l of activated carbon, the fluoride concentration comes below the permissible limit after 1 hour of treatment. The reduction in fluoride concentration thereafter is very minimal. Therefore o.8 g/l can be considered as the optimum dose for treatment.

A major finding of this study is the reduction of pH after treatment. In all the cases the pH concentration falls drastically, making the water highly acidic. This may cause acid mine drainage. The reason for such behaviour has not been found out. Therefore, while carrying

out treatment of fluoride contaminated water in coal mining areas, the neutralization pH is also to be kept in mind.

5.3 Future Scope

This study was limited to the fluoride removal in coal mining areas. It can be extended to other areas as well where problem of fluoride has been reported. A major finding of this study was the reduction of pH after treatment. The reasons for such reduction is to be ascertained with farther scientific study. In future, a detailed may be carried out whereby simultaneous removal of fluoride as well as neutralization pH can be marinated

Chapter 6

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6. REFERENCES

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